

# High Resolution Powder Diffraction Studies of Cadmium-Loaded Zinc-Exchanged Zeolite A.

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**Introduction:** There has been a great deal of interest in the formation of metal clusters encapsulated within the cavities and channels of zeolites due to the potential applications these materials are believed to possess [1]. Crystallographic studies on zinc-loaded zinc-exchanged zeolite A have shown zinc-oxide clusters are formed in the sodalite cages [2]. There have been several studies on cadmium-loaded, cadmium-exchanged zeolite A which show the nature of the clusters formed are highly dependent on the synthetic conditions [3-5]. Recently zinc metal has been loaded into both thallium-exchanged and cadmium-exchanged zeolite X with complicated mixed metal clusters being formed [6-7]. However, to date there have been no attempts to form mixed metal clusters within zeolite A.

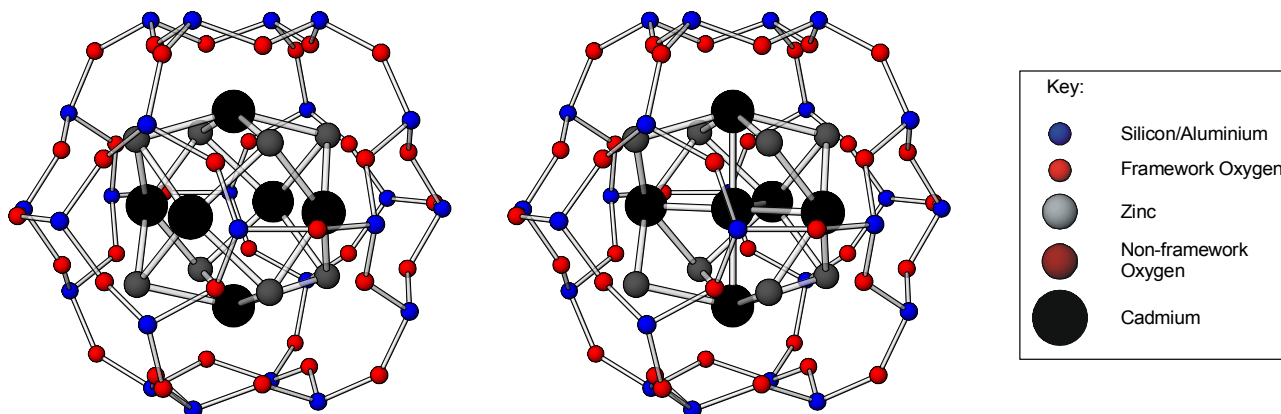
**Methods and Materials:** Zinc-exchanged zeolite A (Zn-A) was prepared by conventional aqueous ion-exchange methods. A quantity of Zn-A was dehydrated at 500°C under vacuum and cadmium metal powder was added under an inert atmosphere. The reaction took place in an evacuated sealed quartz tube at 500°C for 5 days with occasional shaking to maximize homogeneity. At the end of the reaction time a pale yellow colored sample was produced. For diffraction studies to be carried out a small amount of the sample was packed in a 0.7mm glass capillary and sealed with epoxy resin. Diffraction studies were carried out using a wavelength of 0.6857Å.

**Results:** The starting model used was the zeolite framework of dehydrated Zn-A obtained by McCusker and Seff [8]. Least-squares refinement was carried out with the GSAS suite of programs in the space group Pm-3m with a lattice parameter of approximately 12.2Å. After initial refinement, the non-framework atoms were located by means of difference Fourier maps. A combination of bond distances and Fourier map peak sizes were used to assign atoms as cadmium, zinc or oxygen. Inclusion of these sites greatly improved the fit and after refinement of atomic positions, fractional occupancies and isotropic temperature factors convergence was achieved with  $\chi^2=3.905$ ,  $R_{wp}=3.55\%$ ,  $R_p=3.01\%$ ,  $D_{wd}=0.834$  and  $R_F=4.51$ . A combination of bond distances and bond valence sums were used to interpret the results. One zinc atom located in the sodalite cage was also shown to be bonded to a non-framework oxygen. The remaining zinc and cadmium atoms are believed to form two types of  $Zn_8Cd_6^{x+}$  clusters (Figure 1) in 40% of the sodalite cages. Examination of the fractional occupancies showed only half the cadmium metal added was actually encapsulated within the zeolite. The model obtained indicates that the amount of zinc available to form these clusters is dependent on the amount of non-framework oxygen.

**Conclusions:** The results discussed here suggest the possibility of two  $Zn_8Cd_6^{x+}$  clusters in the sodalite cages and to our knowledge constitute only the second reported example of Zn-Cd bonding. As only half the cadmium metal actually became encapsulated within the zeolite, the limiting factor may be the amount of non-framework oxygen in the structure.

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**References:** [1] G. D. Stucky, J. E. MacDougall, *Science*, **247**, 699, 1990. [2] J. E. Readman, I. Gameson, J. A. Hriljac, P. P. Edwards and P. A. Anderson, *Chemical Communications*, 595, 2000. [3] L. B. McCusker, K. Seff, *Journal of the American Chemical Society*, **101**, 5235, 1979. [4] S.B. Jang, U.S. Kim, Y. Kim, K. Seff, *Journal of Physical Chemistry*, **98**, 3796, 1994. [5] A. Goldbach, P.D. Barker, P. A. Anderson, P. P. Edwards, *Chemical Physics Letters*, **292**, 137, 1998. [6] S. Zhen, D. Bae, K. Seff, *Journal of Physical Chemistry B*, **104**, 515, 2000. [7] S. Zhen, K. Seff, *Journal of Physical Chemistry B*, **103**, 6493, 1999. [8] L. B. McCusker, K. Seff, *Journal of Physical Chemistry*, **85**, 405, 1981.



**Figure 1:** The two possible arrangements for  $Zn_8Cd_6^{x+}$  in the sodalite cage.